Quality Assurance Technical Document 8

Bryte Chemical Laboratory Quality Assurance Manual

April 2002

State of California The Resources Agency Department of Water Resources

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The Resources Agency
Department of Water Resources

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Bryte Chemical Laboratory Quality Assurance Manual

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Table of Contents

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1. Introduction

The Bryte Chemical Laboratory's primary role within the Department of Water Resources is to provide analytical, chemical, and biological laboratory services for DWR. As a secondary role, the laboratory provides these same services to other governmental agencies. This manual addresses the quality assurance and quality control measures used by the laboratory in determining the organic, inorganic, and biological entities found in California waters.

This QA Manual addresses all activities that are essential in the operation of the analytical laboratory. The principles presented in this manual are used to ensure the laboratory is providing information that is factual, precise, accurate, reliable, and adequate for its intended use.

This manual is designed to meet the U.S. Environmental Protection Agency policy guidelines as outlined in the *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans,* QAMS-005/80, and also to meet the California Department of Health Services, Environmental Laboratory Accreditation Program.

2. Definition, Purpose, and Scope

Definition of Terms

Quality Assurance Program: An orderly assemblage of management policies, objectives, principles, and general procedures by which an agency or laboratory outlines how it intends to produce data of known and accepted quality.

Quality Assurance: The total integrated program for assuring the reliability of monitoring and measurement data. A system for integrating the quality planning, quality assessment, and quality improvement efforts to meet user requirements.

Quality Control: The routine application of procedures for obtaining prescribed standards of performance in the monitoring and measurements process.

Quality Assessment: The overall system of activities to provide assurance that the QC task is being performed effectively. Quality Assessment involves a continuing evaluation of performance of the production system and the results produced.

Standard Operating Procedure: A detailed written procedure designed to systematize and standardize the performance of the procedure.

Purpose of Manual

The purpose of this manual is to describe the QA/QC Program for all laboratory practices in order to generate the most precise and accurate data possible. To achieve this purpose, a comprehensive and scientifically sound QA Plan has been implemented and is now used.

Scope – Objectives

The ultimate goal of the laboratory is to produce quality data that is accurate, precise, complete, representative, and compatible. While proper validated methodologies are necessary, these alone are not sufficient to assure data quality. The QA Plan is designed to control and monitor laboratory activities, ensuring the laboratory meets the data quality objectives listed above.

This QA Program will be carried out under the direction of the Laboratory QA Officer who reports directly to the Chief of the Bryte Chemical Laboratory. It covers all aspects of sample receiving, storage, preparation, analysis, and reporting.

Standard QC procedures, data reduction, and reporting will be in compliance with requirements in *Standard Methods for Examination of Water and Wastewater*, 19th ed. or later editions. Written SOPs for sample receipt, chain of custody, preservation, storage, preparation, analysis, safety, and reporting shall be followed. Log books, printed documents, data, or other written documentation shall be available to describe the work performed in each of the following stages of analysis:

- Chain of custody
- Sample preservation
- Sample receipt
- Sample storage
- Sample preparation
- Sample analysis
- Data reduction
- Data reporting
- QA/QC

3. Organization and Responsibility

Executing an effective QA program in the laboratory demands the commitment and attention of both management and staff. All laboratory personnel within the organization play a vital role in assuring a continued commitment to the quality of work accomplished. (See Figure 1, Bryte Chemical Laboratory Organizational Chart). The laboratory staff is highly qualified and trained in the following areas:

- Gas chromatography/mass spectrometry (GC/MS)
- Gas chromatography (GC)
- High performance liquid chromatography (HPLC)
- Purge and trap techniques
- Ion chromatography (IC)
- Flame atomic absorption spectroscopy (AA)
- Graphite furnace atomic absorption spectroscopy
- Colorimetric analytical techniques
- Carbon analysis (TOC, TIC)
- Wet chemical analysis
- Analytical method development
- Emission spectroscopy (ICP, ICP/MS)
- Sample preparation
- Fecal coliform
- Chlorophyll and pheophytin
- Phytoplankton

Chief of the Bryte Chemical Laboratory

The Chief of the Bryte Chemical Laboratory is responsible for all operational activities within the laboratory and is accountable for all data generated by the laboratory. QA responsibilities consist of:

- Final review of all data generated by the laboratory
- Final authority to release data to requestor
- Final authority on all analytical procedures and SOPs used by laboratory personnel
- Coordinates with the Laboratory QA Officer in implementing the laboratory QA Plan and its policies, revisions, and any corrective action to ensure compliance
- Periodic audits of the QA Plan to ensure the objectives and procedures are being followed

Laboratory QA Officer

The Laboratory QA Officer is independent and reports only to the Chief of the Bryte Chemical Laboratory. The Laboratory QA Officer:

- Recommends QA policy to the Chief of the Bryte Chemical Laboratory
- Develops and manages the laboratory QA Plan, revises it as needed
- Oversees QC practices in the laboratory and data management
- Helps develop analytical procedures
- Develops precision and accuracy guidelines/criteria
- Reviews data quality in accordance with established guidelines/criteria
- Conducts data quality and laboratory performance audits
- Prescribes and monitors corrective actions
- Recommends QC training for personnel
- Coordinates all QC/QA activities
- Approves SOPs
- Monitors laboratory performance, turn-around, and holding times

Data Control Section

The Data Control Section is responsible for all data coordination and review. Staff performs the following:

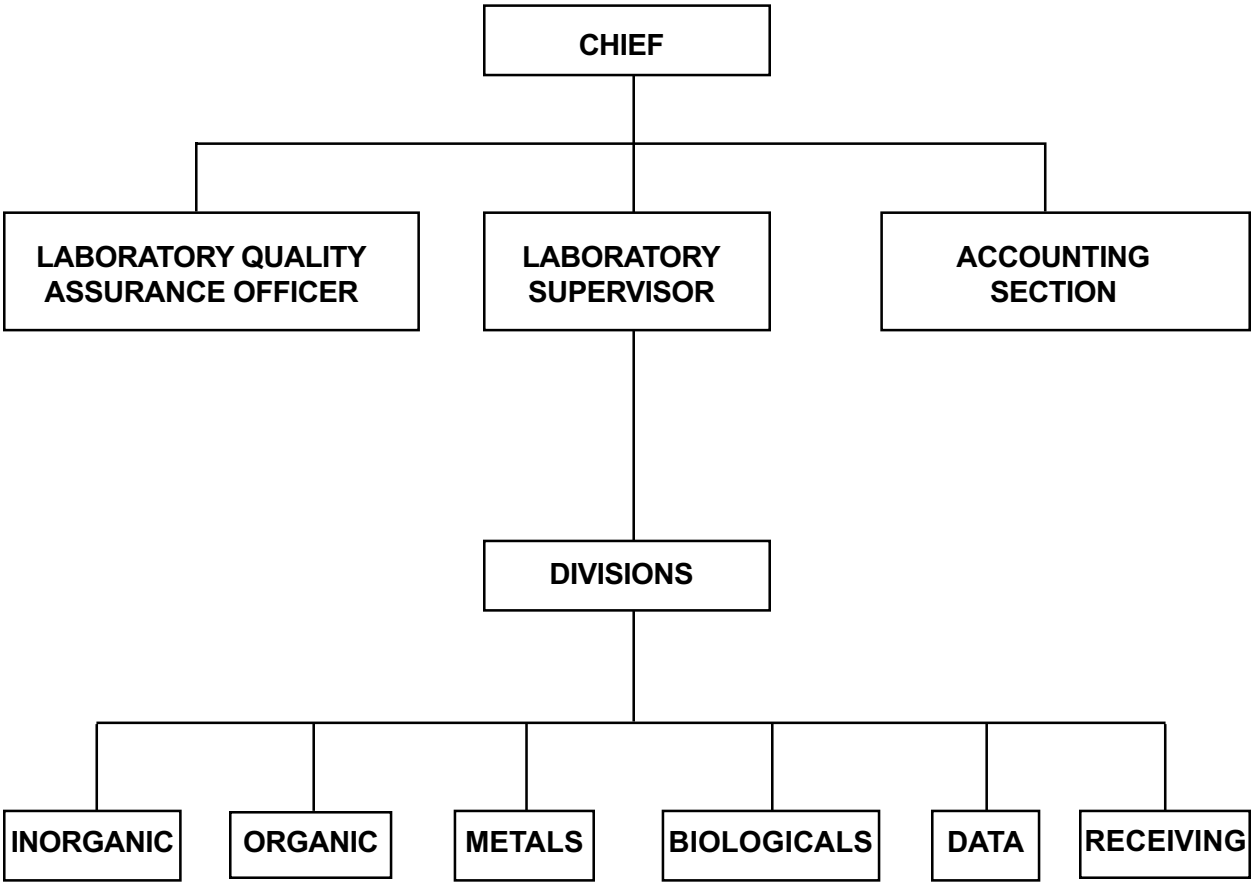
- Reviews all analysis report forms for completeness
- Reviews all analysis request forms to ensure compliance within contractual obligations
- Ensures requestor receives the final completed data report
- Maintains records and archives of all data reports

Laboratory Staff

Since the greatest amount of responsibility for a successful QA Program rests with the analysts, it is important that they be highly qualified and competent. New and experienced laboratory personnel shall be carefully trained for new specific work assignments. Laboratory personnel have on-site access to technical journals and textbooks as well as access to the Resources Agency Library services. Combined administrative and technical staff meetings will be held to help provide a good information exchange forum. Laboratory personnel are responsible for:

- Having a working knowledge of the QA Plan
- Ensuring that all work generated is in compliance with QC acceptance criteria
- Performing all work according to written SOPs
- Ensuring that all documentation to their work is complete and accurate
- Ensuring that acceptance of any data outside QC criteria must be approved by laboratory management
- Maintaining records for all QC data
- Notifying management immediately of any QC issues
- Writing and updating SOPs
- Meeting holding and turnaround times

Figure 1. Bryte Chemical Laboratory Organization Chart



4. Sample Procedures

The laboratory does not take part in any of the actual sampling activities, but the sample collection process is a major concern of the laboratory. Since the ultimate quality of data generated begins with the sampling collection process, the laboratory can assist in the sampling procedure by providing consultation and assistance to project managers and any contractors involved in a project. (See DWR Water Sampling Manual.)

Sample Containers and Holding Times

The laboratory supplies all necessary sampling materials to DWR field sampling units. Using properly cleaned containers and correct preservatives as well as adhering to proper holding times are essential factors for maintaining sample integrity and representativeness. Requirements for sample containers, preservation techniques, and holding times are found in one of the following references (or later editions):

- *Standard Methods for the Examination of Water and Waste Water,* American Public Health Association, et al., 19th Edition, or later
- *Federal Register* Volume 49, No. 209, Friday, October 26, 1984, EPA, 40 Code of Federal Regulations, Part 136
- *Handbook for Sampling and Sample Preservation of Water and Wastewater,* EPA 600/4-82-029, September 1982 (Does not apply to drinking water)

SOPs for cleaning and preparing glassware and sample containers are strictly complied with to ensure that the sample is not contaminated during the collection process due to containers.

Appropriate volumes of the sample must also be collected to ensure that the required detection limits can be met, the QC samples analyzed, and any necessary sample reanalysis performed.

For proper containers, holding times, preservation techniques, and volumes required, see Appendix A (Water Sample Collection Information).

Sample Submittal

Samples are brought to the laboratory by delivery services or field sampling crews. Any sample taken in a nonstandard container, improperly preserved, or shipped in an unacceptable manner may be rejected. Each sample or group of samples needs to be entered into the Field and Laboratory Information Management System. This can be done either manually in the laboratory or in the field and then electronically transferred directly into FLIMS. All pertinent field data is tracked by FLIMS, such as the date, time, location, field sampler, field data, laboratory tests requested, etc. When the samples are completely logged in, FLIMS notifies the laboratory personnel that samples need to be analyzed.

Sample Storage and Handling

The samples received by the laboratory are placed in appropriate storage or sent directly to the test area. The storage areas are located in the Receiving Room and consist of refrigerators at 4^{o}C, freezers at -10^{o}C, and designated storage cabinets for sample types, (i.e., metals, standard minerals, etc.). Once the analysis is completed, the remaining sample is kept for 30-60 days in storage, then discarded. If a contracting officer should request return of a sample prior to the expiration interval, it will be returned in a manner that meets the required criteria.

Quality Assurance Sample

To evaluate and ensure acceptable results, the laboratory requires that samplers submit with their samples travel blanks, field blanks, and/or duplicate samples. For specific requirements, see DWR Water Quality Sampling Procedures.

5. Sample Custody Procedures

A Chain of Custody form must be completed for samples received by the laboratory which may be used as evidence for enforcement purposes. Once a sample is received, the Chain of Custody Officer or the alternate is notified. All information is then transcribed to the Chain of Custody form and the sampler signs the form, witnessed by the Chain of Custody Officer or alternate. The sample is then transferred to the appropriate location to wait for analysis. For each transfer of physical custody, an entry of disposition and one of receipt is made on the custody form.

While in the laboratory, samples are stored in secure areas under appropriate preservation and environmental conditions. Following the completion of the analysis, the samples are stored until the results are submitted to the Program Manager and permission to discard has been received. A notation of completion is made on the Chain of Custody form, and the document is then filed with the analysis report. Copies of the files are maintained in DWR's archives.

6. Calibration and Measurement Procedures

Calibration of instruments is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity to meet established detection limits. In general, calibration is accomplished by measuring instrument response to standards containing the analytes in known concentrations while being in compliance with manufacturer's recommendations.

Instrument Calibration and Frequency

Today's complex instrumentation and calibration frequencies are extremely varied; therefore, a bound notebook is assigned to each instrument to log the following:

- All maintenance performed
- All daily sensitivity checks and/or calibration results where applicable according to methodology found in SOP
- All manufacturer's maintenance and repairs

Each log entry will contain the date, operator's name, and operation performed (i.e., maintenance, sensitivity check, etc.).

Calibration is accomplished on a daily basis or whenever the following instruments are used:

- Atomic Absorption (flame and furnace)
- Spectrophotometers
- Gas-Liquid Chromatographs
- Ion Chromatographs
- Mass Spectrometers
- Auto Titrators
- Auto Analyzers
- Atomic Emission (ICP and ICP/MS)

Other instruments may require weekly, monthly, quarterly, or even semiannual calibration (i.e., balances, ovens, exhaust hoods, etc.). Once a standard calibration range has been established, at least three standards are normally used in daily standardization where applicable. For specifics, see the SOP for a particular analytical procedure. If a problem arises which cannot be corrected by the instrument operator, then the Laboratory QA Officer is notified. The officer will coordinate the necessary diagnostic and corrective measures to be implemented. Documentation will be provided in the instrument log book.

Calibration Standards/Reagents Preparation

A critical area in the generation of quality data is the quality, purity, and traceability of the standards and reagents used in analytical calibration procedures. All primary reference standards and standard solutions used by the laboratory are obtained from the National Institute of Standards and Technology or commercial manufacturers. All standards, standard solutions, and reagents are validated prior to being used. Validation procedures range from a check for chromatographic purity to verification of concentration of the standard using standards prepared at a different time or from a different source.

All Stock Standards are labeled as to the following:

- Name and Concentration of Stock
- Method of Preparation
- Date Prepared/Preparer's Name
- Supplier, Purity, Lot Number, and Expiration Date
- Any other pertinent information

New working standards are compared to the remainder of the current working standards for any concentration differences, formation of precipitates, and any signs of deterioration. Reagents are also examined for purity by subjecting an aliquot to the analytical method for its intended use. For example, reagent water, organic solvents, or acids are analyzed for possible contamination prior to use.

7. Analytical Procedures

Analytical methods are derived from the latest editions of one of the following references:

- *Methods for Chemical Analyses of Water and Wastes*, EPA-600/4-79-020 (revised March 1983) (Not used for drinking water.)
- *Standard Methods for the Examination of Water and Wastewater*, 19th Edition or later, APHA, American Water Works Association, Water Pollution Control Federation, Washington, D.C. (1992)
- *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water Resources Investigations,* USGS, Book 5, Washington, D.C. (1985)
- *Annual Book of American Society for Testing and Materials Standards*, Volumes 11.01 and 11.02, ASTM, Philadelphia, Pennsylvania (1988)
- *Official Methods of Analysis,* 14th Edition, AOAC International, Arlington, Virginia (1984)
- *Methods for Organic Chemical Analysis of Municipal and Industrial Wastes*, EPA 600/4-82-057, (1982)
- *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under Clean Water Act,* Federal Register, EPA, 40 CFR, Part 136, (1984)
- *Biological Field and Laboratory Methods*, EPA-670/4-73-001, (1973)
- *Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods*, EPA, SW846, Volumes 1A, 1B, 1C, and II, (1986)

For a specific analytical method used, see Appendix F.

Standard Operating Procedure

Analytical methods chosen are dependent upon certain objectives, some of which consist of precision and accuracy, type of sample matrix, and quantitative sensitivity. Each analytical method routinely used is documented in the form of a SOP which contains complete detailed instructions to standardize the expected performance of the analytical method. Contents of a laboratory SOP are given in Appendix B. Any deviations from published methodology are documented in the SOP.

Analytical Methodology Verification

Before any analytical method is routinely used to generate data, the method is validated. Criteria used to validate a method consist of the following:

- Method selection by senior staff
- Testing of method verifying reporting limits, dynamic range, matrix effects, precision, and accuracy criteria
- Data acceptance criteria must be approved by the Laboratory QA Officer and Chief of the Bryte Chemical Laboratory
- Final documentation of the method in a written SOP

8. Data Reduction, Validation, and Reporting

The final step in analyzing samples is to review the data collected prior to reporting. The analytical data generated within the laboratory are extensively checked and cross-checked for their accuracy, precision, and completeness. The validation process consists of data generation, reduction review, and finally reporting results to the submitter.

The primary responsibility for the generation of accurate data rests with the analyst. The analyst performs the data calculation functions and is responsible for the initial examination of the finished data. All data reduction steps applied to the raw data are outlined in the appropriate analytical SOPs. Each analyst reviews the quality of their work based on the following guidelines:

- The appropriate SOP has been followed
- Sample preparation is correct and complete
- Analytical results are correct and complete
- Blank correction procedures are followed, if applicable
- QC samples are within established QC limits
- All documentation is complete, including analysis report, QC form, and QC charts

The QC procedures outlined in the analytical SOP are used for the preliminary validation of the results along with any historical data, if available. When applicable, correlation checks are used to validate the data, such as anion-cation balances, specific conductance versus dissolved solids, dissolved solids versus calculated dissolved solids, Biological Oxygen Demand versus suspended solids, Chemical Oxygen Demand or Total Organic Carbon, etc. After data reduction and validation steps are computed, the analyst enters the data into the FLIMS and releases the QC batch.

The data package is then forwarded electronically in the FLIMS to the QA Officer, who evaluates the data along with all pertinent QC results such as laboratory control standards, matrix spikes, surrogates, duplicates, blind duplicates, blind Performance Evaluation samples, and laboratory performance records, as well as historical records to help form a basis for acceptance of data. If the data package passes QA/QC criteria, it is released in the FLIMS to the senior staff.

A data package containing the required QC batches for each sample submittal is then reviewed by senior staff for final validation, completeness, and acceptance. The final review is based on the following criteria:

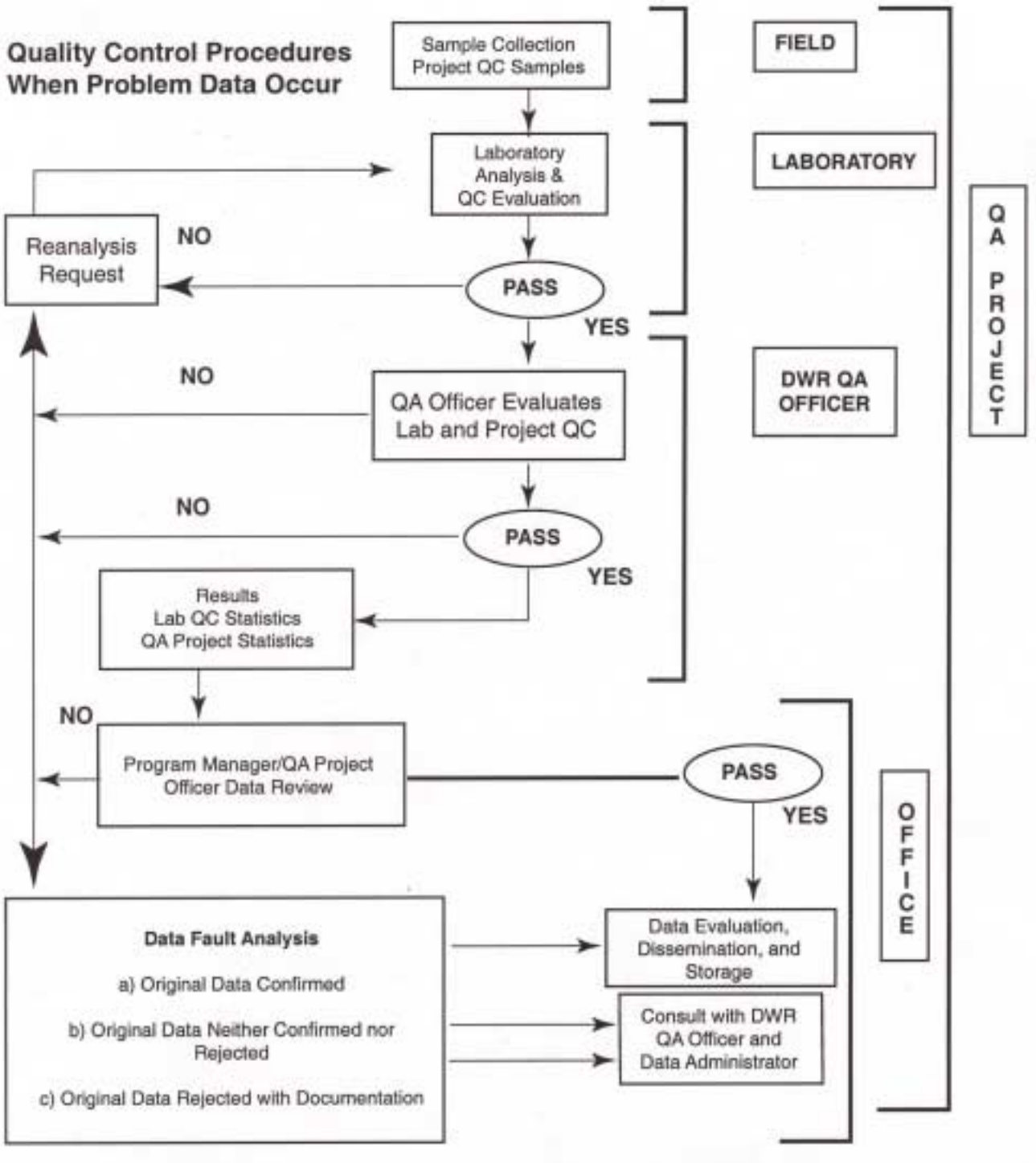
- Calibration data reviewed
- Appropriate methodologies used
- QC samples within established guidelines
- Comparison of historical data when available
- Correlation checks reviewed (i.e., anion-cation balance, electrical conductivity versus total dissolved solids, etc., when applicable
- Evaluation of data in general by comparability, assessment, and reasonableness of sample types, (i.e., wastewaters, surface waters, groundwaters, etc.)
- Ensures completion of all analytical work requested

After validation and review by senior staff, the approved data package is incorporated into a final analysis report. The final report is released to the submitter either in a printed format with all the appropriate information or sent to the submitter by FLIMS in electronic format. The full data package is then archived for possible future use.

Errors or problems which may occur are documented and transmitted to the appropriate section. The cause of the errors is then addressed either by further training or reevaluation of the analytical method SOPs to ensure quality data are generated at the analyst level.

See Figure 2. Data Validation Flowchart on the following page.

Figure 2. Data Validation Flowchart



9. Internal Quality Control Checks

Internal QC is the routine activities and checks such as calibrations, duplicate analysis, spiked samples, etc. included in normal procedures to control accuracy and precision of the measurement process. It determines whether the laboratory operations are within acceptable QC guidelines during data generation.

Blanks

Field Blanks are check samples which monitor contamination originating from the collection, transport, and storage of environmental samples. Laboratory prepared blank water is supplied to field personnel for processing in the same manner as samples; this includes field filtration and addition of preservatives.

Travel Blanks are prepared in the laboratory from ultrapure water. They are supplied to field personnel with each batch of empty sample bottles and are returned with the collected samples. Travel blanks are routinely used for volatile organic samples to determine whether sample transport has contaminated the samples collected.

Method Blanks are prepared from laboratory blank water, substituted for samples, and analyzed with every sample set. Method blanks are used to determine the level of contamination that exists in the analytical procedure. Contamination may or may not lead to elevated concentration levels or false positive data. Ideally, the concentration of an analyte in the method blank is below the method detection level for the analyte. However, for some analytical methods, elimination of blank contamination is extremely difficult; therefore, each analytical SOP has a method blank level of acceptance. If the acceptance contamination level is exceeded, the sample set is reanalyzed.

Calibration Standards

Calibration standards are routinely run with every sample set. Calibration standards must fall within certain QC limits before any sample results can be accepted. The limits are found in the particular analytical method SOP being used. If the calibration standards are unacceptable, the sample results are rejected, corrective action taken, and the samples reanalyzed.

Check Standards

The check standard is usually a midrange calibration standard used to monitor the analytical method. The check standard is analyzed every ten samples to provide evidence that the laboratory is performing the method within accepted QC guidelines. As long as check standard results fall within established control limits, the analysis can continue. If check standard results fall outside the control limits, the data are suspect and the procedure is stopped. The analytical procedure is checked for error step by step by the analyst. Once the procedure is again acceptable, reanalysis of samples begins with the last check standard that was within acceptable control limits.

Laboratory Control Sample

When one is available, the LCS is analyzed routinely to verify the analytical method is in control and to also serve as a second source verification for the calibration standards of all routine analyses. The concentration of the LCS is within the working range of the analytical method and does not require extensive pretreatment, dilution, or concentration prior to analysis. The sources include, but are not limited to: QC samples, EPA, commercially prepared samples, or samples prepared in-house with different sources than those used in the calibration standards. Recovery data from the LCS are compared to the control limits which are established for those analytes monitored by the LCS. Before any data can be accepted, the analytes of interest must fall within their expected control limits. If, for any reason, the results fall outside those limits, the sample results are unacceptable. Corrective steps are taken and filed with the QA/QC Officer. After the corrective action has been proven effective and the LCS is within the specified control limits, the samples are then reanalyzed.

Internal Standards

An internal standard is used for the quantitation of organic compounds by gas chromatography (GC) or a combination of gas chromatography and mass spectrometry (GC/MS). The internal standard is similar in analytical behavior to the compounds of interest and is added to all samples, standards, and blanks. Usually, more than one internal standard is added to each sample to evaluate the measure-

ment of the sample throughout the entire time of analysis. The internal standards help determine the individual response factors used to calculate the concentrations of the organic compounds of interest.

$$RF = (A_s)(C_{is})/(A_{is})(C_s)$$

where:

A_s = Area for reference analyte to be measured

A_{is} = Area for the internal standard

C_{is} = Concentration of the internal standard (µg/L)

C_s = Concentration of the reference analyte to be measured (µg/L)

$$C_s = (A_s/A_{is})(C_{is}/RF)$$

where:

C_a = Concentration of the analyte in sample in µg/L

A_a = Peak area of the analyte

RF = Response Factor

The monitoring of the internal standards area counts and retention times are also used as a continuing check on system performance. An average retention time/area count is established for each internal standard. In any analytical run in which the internal standard retention time/area count falls outside the established criteria, the run is aborted, the cause is corrected, and the sample is reanalyzed.

Surrogate Compounds

Surrogate compounds are used in the analysis of organic compounds by gas chromatography (GC) and/or by a combination of gas chromatography and mass spectrometry (GC/MS) in conjunction with the internal standards mentioned above. Like the internal standard, the surrogate compounds are similar in analytical behavior to the compounds of interest and are added to all samples, standards, and blanks. A known amount of surrogate is added to monitor the analytical performance of the method. The results of the surrogate compounds must fall within the established QC criteria for recoveries and retention times for the analytical method. This helps to ensure the data generated meet QA objectives for that analytical method.

Sample Duplicates

Duplicates are environmental samples divided into two separate aliquots analyzed independently to determine the repeatability or precision of the analytical SOP. The difference in the duplicate results must be within established control limits to ensure the generated data meet the quality assurance objectives for the particular analytical method.

Matrix Spike/Matrix Spike Duplicates

A spiked environmental sample is used to check for any matrix effects on the precision and accuracy of an analytical measurement. One out of every 20 samples or one per batch is spiked twice with a known concentration of the analyte of interest, then analyzed in a normal manner. The percent recovery and relative percent difference are calculated and the results must fall within established control limits to ensure the generated data meets the QA objectives for the particular analytical method used.

Performance Evaluation Samples

PE samples are routinely issued to the analyst to monitor both the analyst's work and analytical procedure SOP. The recorded results are reviewed by both the Laboratory QA Officer and senior staff. If any problems occur, follow-up corrective action is taken. PE samples may be in the form of blanks, previously analyzed environmental samples, split samples, or standard reference materials such as EPA, USGS, etc.

Standard Method of Additions

Standard method of additions is the practice of adding known concentrations of analyte to a sample so that matrix effects (interferences) are minimized. Whenever sample interference is suspected, the method of standard additions is employed to verify the quality of the data.

Bracketing

Bracketing is the use of standards to bracket the apparent concentration of the analyte in the sample. The sample is bracketed between a high and low standard, the standards being as close to the measured sample value as possible, usually ±10 percent. The calculated results are then done by interpolation as follows:

$$C_s = [((R_s-R_{ls})(C_{hs}-C_{ls})/(R_{hs}-R_{ls}))+C_{ls}](\text{dilution})$$

where:

C_s = Sample Concentration

R_s = Response of Sample

R_{hs} = Response of High Standard

R_{ls} = Response of Low Standard

C_{hs} = Concentration of High Standard

C_{ls} = Concentration of Low Standard

Normally, bracketing is used where precision of the methodology is poor. By bracketing, verification of data quality can be obtained.

10. Performance and System Audits

Performance and System Audits are an essential part of QA to ensure that the laboratory is statistically generating consistent valid data. A system audit consists of reviewing laboratory conditions, practices, equipment, staff, and procedures used to generate quality data. Performance audits verify the ability of the laboratory to correctly identify and quantitate compounds in blind check samples. The laboratory currently participates in several ongoing auditing programs on a regular basis. The audits can be categorized into external and internal audits.

External Audits

The laboratory participates in the following external audit programs:

- Water Pollution\Supply Performance Evaluation Studies, U.S. Environmental Protection Agency
- Standard Reference Water Sample Project, U.S. Geological Survey
- San Joaquin Valley Drainage Program interlaboratory comparison studies
- Split sample analysis with other laboratories both public and private

Internal Audits

Regular audits using an in-house blind reference sample are conducted for specific routine procedures. The results of these analyses are evaluated by the Laboratory QA Officer and Chief of the Bryte Chemical Laboratory. System audits are conducted to assess the QA implementation in the laboratory. Inspection of QC charts, analytical procedures, equipment logs, and QA documentation in general is evaluated and reviewed for compliance and any needed operational changes. In addition, informal audits are conducted by the Laboratory QA Officer as required when accuracy and precision of analyses appear to be drifting out of control. These audits may include the use of QC samples, varied matrices, calibration of instruments, and observation of the analyst to identify additional training or clarification needs, and may require changes in the analytical SOP.

The control limits calculated for the Range (Duplicates) and Percent Recovery (Spikes) are based on the following equations:

Range

- $\bar{R} = |A - B|$
- $\bar{R} = \left(\sum R\right) / n$, *when* $n =$ *minimum* 20 *duplicate pairs.*
- *Upper control limits,* $UCL = 3.327\ (\bar{R})$
- *Warning Limit* $= 2.456\ (\bar{R})$

Percent Recovery

- $\%R = \dfrac{(\text{sample} + \text{Spike}) - \text{sample}}{\text{Spike}} \times 100$
- n = minimum of 20 spiked percent recoveries
- $x = (\Sigma\ \%Rec)/n$
- Std. deviation $(S_d) = \sqrt{\dfrac{n(\Sigma x^2) - (\Sigma x)^2}{n(n-1)}}$
- Upper Control Limit, UCL $= x + 3S_d$
- Lower Control Limit, LCL $= x - 3S_d$
- Upper Warning Limit, UWL $= x + 1.5S_d$
- Lower Warning Limit, LWL $= x - 1.5S_d$

11. Preventive Maintenance

Preventive maintenance is routinely performed on all analytical equipment and instruments to minimize the amount of downtime and to maintain data quality. Equipment manuals, troubleshooting guides, and log books are available for maintenance support. Critical spare parts are kept on hand for laboratory instrumentation that is routinely repaired by laboratory staff. This inventory is monitored and maintained to avoid extended periods of downtime.

Service Contracts

The laboratory maintains service contracts with manufacturers and specialty companies for complex analytical equipment (i.e., GC and ICP/MS).

General Maintenance

Instrument operators are responsible for routine daily maintenance such as cleaning external optics, making adjustments in focus, needing sampler probes, etc. and for maintaining the equipment log books. Designated laboratory personnel are trained and responsible for more complex maintenance procedures. All necessary repairs are performed by trained staff or factory service engineers. The Chief of the Bryte Chemical Laboratory will be informed of the need for, and the performance of, all major maintenance activities, where these activities may directly impact sample analysis schedules.

Equipment Log Books

Equipment log books are maintained for all analytical instruments and equipment used in the laboratory. Each entry in the log book includes the date, the nature of the entry, and the name of the individual responsible for the entry. The following information is recorded in the log books:

- Results of all sensitivity checks (verifying the equipment is operating according to QA criteria for the method and/or meets the manufacturer's specifications)
- All scheduled maintenance performed
- Any major or minor problem encountered, a brief description, corrective action required, and a list of any parts replaced
- Verification of equipment operation after any maintenance is performed by designated laboratory staff

The equipment log books are periodically reviewed for compliance and problem areas in the equipment by the Laboratory QA Officer.

12. Routine Procedures Used to Assess Data Quality

The effectiveness of data quality assessment in a QA program is measured by the quality of data generated by the laboratory. Data quality is evaluated in terms of precision, accuracy, comparability, and completeness.

Precision and Accuracy

Precision is the degree to which the measurement is reproducible among replicate observations, and accuracy is a determination of how close the measurement is to the true value. Laboratory precision and accuracy have been established for all analytical procedures used and are assessed for each sample set that is analyzed. The precision of analytical data is determined routinely by running duplicate tests on samples, laboratory control standards, and matrix spikes within the sample set. Accuracy is evaluated by analysis of spiked samples. Sample spikes are prepared by addition of a known amount standard solution to a sample. The spiked sample and unspiked sample are then analyzed for the parameter of interest. Precision and accuracy assessment utilize control charts and well established statistical procedures found in the following reference publications:

- *Handbook for Analytical Quality Control in Water and Wastewater Laboratories* (EPA 600/4-79-019, March 1979)
- *Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments, Techniques of Water Resources Investigations*, USGS, Book 5, Chapter A6, 1982
- *Manual of Analytical Quality Control for Pesticides and Related Compounds in Human and Environmental Samples* (EPA-600/1-79-008, January 1979)

Comparability

Comparability expresses the confidence with which the data set can be compared to other data sets measuring the same properties. See Section 8.1, Data Validation and Reporting, for procedures used to evaluate comparability for assessment of data quality.

Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. For data quality assessment procedures used to evaluate the completeness of data, see Section 8.1, Data Validation and Reporting.

Detection Limits

The sensitivity of any analytical method is related to the detection limits, the lowest concentration of analyte that can be detected at a specified confidence level. Definitions of Instrument Detection Limit, Method Detection Limit, Method Quantification Limit, and Practical Quantification Limit follow. The relationship of these terms is expressed graphically in Figure 3.

Instrument Detection Limit

Definition: The smallest signal above background noise that the instrument can detect reliably at 99 percent confidence level.

Measurement: Analyze replicate blank samples to determine the extent which the analyte signal exceeds the peak-to-peak noise.

Calculation: The mean value plus two standard deviations for a normal distribution or three for data distribution.

Method Detection Limit

Definition: The lowest possible concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing analyte.

Measurement: Analyze several replicates of a sample, digestate, or extracted sample with no detectable analyte to establish the estimated MDL. Prepare a concentration between three to five times the estimated MDL. Analyze seven aliquots and process each through the entire analytical method then calculate the standard deviation.

Calculation: (Sd)

$$Sd = \sqrt{\frac{n(\sum x^2)-(\sum x)^2}{n(n-1)}}$$

From a table of the one-sided (t) distribution select the value of (t) for 7-1=6 degrees of freedom at the 99 percent level; this value is 3.143. The following relationship is used to calculate the MDL:

MDL = 3.143 (Sd)

Practical Quantification Limit

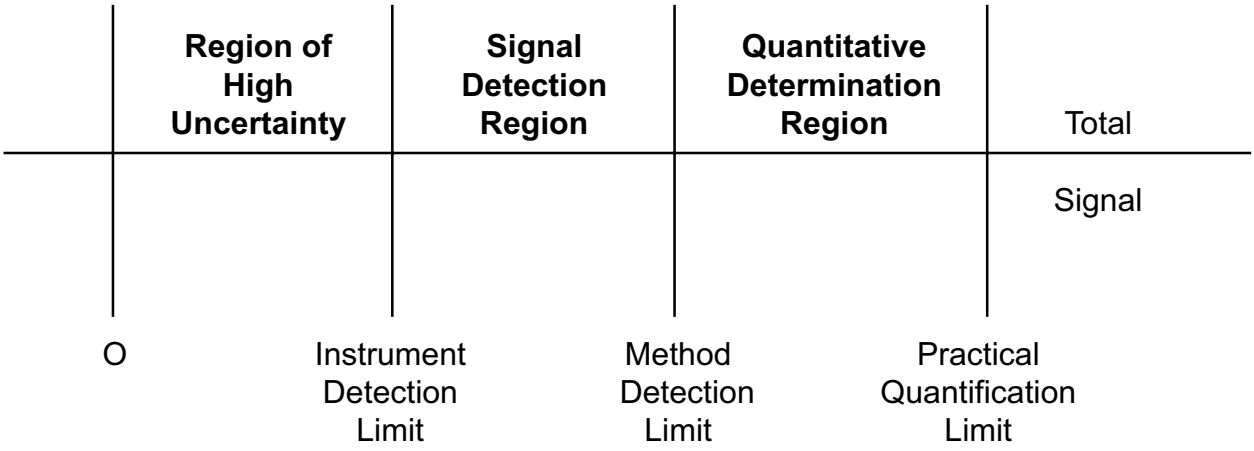
Definition: The minimum level that can be reliably achieved by the analytical method within specified limits of precision and accuracy during routine laboratory operating conditions.

Measurement: The PQL is 5 to 10 times the MDL.

Reporting Limits

The reporting limit is the PQL value of the specific analytical method, for specific reporting limits see Appendix F.

Figure 3. Graphical Representation of Detection Limits



Relationships shown are not meant to indicate any absolute signal values.

13. Corrective Action

When errors, deficiencies, or out of control conditions are encountered, corrective actions are necessary. The need for corrective action may be identified in any number of ways:

- QC data outside acceptable limits for a given sample set
- Rising or falling trends that are detected in spike recovery or duplicate control charts
- Unacceptable levels of contamination in blanks and reagents
- Unusual changes in detection limits
- Calibration standards with low sensitivity
- Nonlinear or misshapen calibration curves
- Deficiencies detected by Laboratory QA officer or senior staff reviewing analytical data
- Deficiencies detected during internal or external audits by Laboratory QA Officer, outside agency, or from performance evaluation studies

Since each analytical SOP has a QA Section that outlines corrective actions to be taken, problems which may arise are usually handled at the analyst's level. If the problem persists and cannot be handled by the analyst, the matter is referred to the Laboratory QA Officer. The following corrective action steps are then taken:

- Identification of the problem
- Investigation and determination of the cause of the problem
- Corrective action determined to eliminate the problem
- Assigning responsibility for implementing corrective action
- Evaluation of the effectiveness of the corrective action
- Verification that the corrective action has eliminated the problem
- Documentation of the problem and corrective action needed

All suspect analytical results will be evaluated. The Laboratory QA Officer will not permit the analysis to go on-line until the corrective action has been completely successful. Corrective action documentation is routinely reviewed by the Laboratory QA Officer and Chief of the Bryte Chemical Laboratory for recurring problems which may require changes in analytical procedures, methods, or additional training of analysts.

14. Quality Assurance Reports

QA Reports are generated by the Laboratory QA Officer with assistance from senior staff. These reports are used in evaluating the overall QA Program, identifying problems and trends, and planning for future needs and requirements. These reports will usually include the following:

- All audit results including any necessary corrective action required
- Performance evaluation results and commentary
- Problems encountered and corrective action taken
- Any significant QA problems encountered
- Comments and recommendations

External reference samples from USGS, USEPA, DHS, or University of California, Davis are analyzed a minimum of three times per year. A QA report is generated after each external reference is completed. If special problems arise involving more than normal corrective action, a special QA Report will be issued. The reports will be routed to specific staff members and finally, the Chief of the Bryte Chemical Laboratory.

15. Facilities and Laboratory Equipment

The Bryte Chemical Laboratory, located in West Sacramento, California, contains a fully equipped 8,700-square-foot facility. The fully air conditioned laboratory contains one large main room and smaller individual rooms with adequate hood area appropriately spaced and sufficient room to accommodate all personnel and equipment. The laboratory is divided into sections to handle the wide spectrum of chemical analyses performed on waters and wastewaters. The major sections consist of receiving, volatile organics, semi-volatile organics, trace metals, wet chemistry, nutrients, biological, and storage. Most of the instrumentation used in the chemical laboratory is fully automated and computerized. (See Appendix H, Laboratory Equipment.)

Appendix A
Water Sample Collection Information

Water Sample Collection Information

Determination	Method	Container	Sample Prep	Sample Size	Preservative	Hold Time
Alkalinity	SM 2320B	Polyethylene	Filtered	500ml	4°C	14 days
BOD	EPA 405.1	Polyethylene	Unfiltered	2000ml	4°C	48 hours
Carbamate Pesticides	EPA 531.1	Glass, Clear	Unfiltered	125ml, teflon septa	4°C, chloroacetic acid	28 days
COD	SM 5220A	Glass, Clear	Unfiltered	100ml	4°C, H2SO4, pH<2	28 days
Chlorinated Pesticides	EPA 608	Glass, Amber	Unfiltered	1000ml, teflon septa	4°C	7d ext, 40d after ext
Chlorinated Phenoxyacid Herbicides	EPA 615	Glass, Amber	Unfiltered	1000ml, teflon septa	4°C	7d ext, 28d after ext
Chlorophyll	SM 10200 H	Manila Envelope	Filtered	1000ml	-20° C, dark	28 days
Chromium, hexavalent	EPA 218.6	Glass, Clear VOA	Unfiltered	40ml	4°C	24 hours
Coliform, Fecal (Escherichia)	SM 9223 Colilert	Plastic, Sterile	Unfiltered	100ml	4°C, Na2S2O3	6 hours
Color	EPA 110.2	Polyethylene	Filtered	500ml	4°C	48 hours
EDB/DBCP	EPA 504	Glass, Amber VOA	Unfiltered	40ml X 2, teflon, no air	4°C, HCL, pH<2	28 days
Electrical Conductivity (EC)	SM 2510B	Polyethylene	Filtered	500ml	4°C	28 days
Glyphosate	EPA 547	Glass, Amber	Unfiltered	125ml, teflon septa	4°C	28 days
Haloacetic Acids (HAA)	EPA 552.2	Glass, Amber VOA	Unfiltered	40ml X 2, teflon, no air	4°C	7d ext, 14d after ext
Haloacetic Acids Formation Potential (HAAFP)	EPA 510.1	Glass, Amber VOA	Filtered	40ml X 3, teflon, no air	4°C	7d ext, 14d after ext
Hardness by Calculation	SM 2340B	Polyethylene	Filtered	250ml	HNO3, pH<2	6 months
Hardness, Total by Calculation	SM 2340B	Polyethylene	Unfiltered	250ml	HNO3, pH<2	6 months
ICP Cations, Dissolved - Na,Ca,Mg, K, B, Si	EPA 200.7	Polyethylene, Acid Washed	Filtered	250ml	HNO3, pH<2	6 months
ICP Cations, Total - Na,Ca,Mg, K, B, Si	EPA 200.7	Polyethylene, Acid Washed	Unfiltered	250ml	HNO3, pH<2	6 months
ICP/MS Trace Metals, Dissolved	EPA 200.8	Polyethylene, Acid Washed	Filtered	500ml	HNO3, pH<2	6 Months
ICP/MS Trace Metals, Total	EPA 200.8	Polyethylene, Acid Washed	Unfiltered	500ml	HNO3, pH<2	6 Months
IC Anions - CL, SO4, Br, F	EPA 300.0	Polyethylene	Filtered	500ml	4°C	28 days
Mercury by Cold Vapor	EPA 245.1	Polyethylene, Acid Washed	Unfiltered	500ml	4°C, HNO3, pH<2	28 days
Mercury by ICP/MS	EPA 200.8	Polyethylene, Acid Washed	Filtered	500ml	4°C, HNO3, pH<2	28 days
Methylene Blue Active Substances (MBAS)	EPA 425.1	Polyethylene	Unfiltered	500ml	4°C	48 hours
Nitrate, Nitrite (Nutrient)	SM 4500-NO3-F	Polyethylene	Filtered	250ml	-20° C, dark	48 hours
Nitrate, Nitrite (Nutrient DWR Modified)	SM 4500-NO3-F DWR	Polyethylene	Filtered	250ml	-20° C, dark	28 days

Water Sample Collection Information

Determination	Method	Container	Sample Prep	Sample Size	Preservative	Hold Time
Nitrate, Nitrite (Std Mineral-IC Anions)	EPA 300.0	Polyethylene	Filtered	500ml	4°C	48 hours
Nitrate, Nitrite (Std Mineral DWR Modified)	EPA 300.0 DWR	Polyethylene	Filtered	500ml	4°C	28 days
Nitrogen/Phosphorous Pesticides	EPA 614	Glass, Amber	Unfiltered	1000ml, teflon septa	4°C	7d ext, 40d after ext
Nitrogen, Ammonia	EPA 350.1	Polyethylene	Filtered	250ml	-20° C, dark	28 days
Nitrogen Kjedahl, Total (TKN)	EPA 351.2	Polyethylene	Unfiltered	250ml	-20° C, dark	28 days
Nitrogen Organic, Dissolved (DON)	EPA 351.2	Polyethylene	Filtered	250ml	4°C	28 days
Oil and Grease	EPA 1664	Glass	Unfiltered	1000ml	4°C, H2SO4, pH<2	28 days
Organic Carbon Dissolved (DOC)	EPA 415.1(D)	Glass, Clear VOA	Filtered	40ml	4°C, H3PO4, pH<2	28 days
Organic Carbon Total (TOC)	EPA 415.1(T)	Glass, Clear VOA	Unfiltered	40ml	4°C, H3PO4, pH<2	28 days
Orthophosphate	SM 4500-P-F	Polyethylene	Filtered	250ml	4°C	48 hours
Orthophosphate DWR Modified	SM 4500-P-F DWR	Polyethylene	Filtered	250ml	-20° C, dark	28 days
pH	EPA 150.1	Polyethylene	Unfiltered	250ml	4°C	0.25 hours
Phosphorous Total	EPA 365.4	Polyethylene	Unfiltered	250ml	-20° C, dark	28 days
Simulated Distribution Sytem THM	SM 5710C SDS-THM	Glass, Amber VOA	Filtered	40ml X 3, teflon, no air	4°C	7 days after FP
Simulated Distribution Sytem HAA	SM 5710D SDS-HAA	Glass, Amber VOA	Filtered	40ml X 3, teflon, no air	4°C	7d ext, 14d after ext
Solids, Settleable	EPA 160.5	Polyethylene	Unfiltered	2000ml	4°C	7 days
Solids, Total Dissolved (TDS)	SM 2540C	Polyethylene	Filtered	500ml	4°C	7 days
Solids, Total Suspended (TSS)	EPA 160.2	Polyethylene	Unfiltered	500ml	4°C	7 days
Solids, Volatile Suspended (VSS)	EPA 160.4	Polyethylene	Unfiltered	500ml	4°C	7 days
Trihalomethanes (THMS)	EPA 501.1	Glass, Amber VOA	Unfiltered	40ml X 2, teflon, no air	4° C, HCl, pH<2	14 days
Trihalomethane Formation Potential (THMFP)	EPA 510.1	Glass, Amber VOA	Filtered	40ml X 3, teflon, no air	4°C	7 days after FP
Turbidity	EPA 180.1	Polyethylene	Unfiltered	500ml	4°C	48 hours
UVA	SM 5910B	Polyethylene	Filtered	250ml	4°C	14 days
Volatile Organic Analysis (VOA)	EPA 502.2	Glass, Amber VOA	Unfiltered	40ml X 2, teflon, no air	4° C, HCl, pH<2	14 days

Appendix B
Standard Operating Procedure

Analytical methods SOP must include:

1. Title
2. Scope and application
   - 2.1 Analytes
   - 2.2 Reporting limits
   - 2.3 Applicable matrices
   - 2.4 Calibration range
   - 2.5 Analysis time
3. Method summary
4. Comments (interference or helpful hints)
5. Safety issues
6. Sample collection, preservation, containers, and holding times
7. Apparatus
8. Reagents and Standards
9. Procedure
10. QA/QC requirements (QC samples, acceptance criteria, and corrective action)
11. Calculations
12. Reporting requirements (units, limits, significant figures, data entry)
13. References (method source, deviations from method source, and rationale for deviation)
14. Additional information as appropriate

Appendix C
Sample Labeling Requirements

A. Label must be written with waterproof ink.

1. Directly on sample container
2. On gummed label
3. On attached sample tag

B. Label information requested when applicable

1. Sample number
2. Sample type (either by name or code number) i.e., metal, mineral, pesticide, biological, Code 7, etc.
3. Date sample collected
4. Location of sample
5. Filtered or unfiltered
6. Fixed (acidified)

C. Examples of label information used includes:

N04217	FQ03112	D08112
Nutrient	Metals	Method code 1
Unfilt.	Fixed & Filt.	Filtered
Clear Lake, Bot.	HMH2462, sump.	Bryte Bend
2/20/98	3/12/98	4/29/98

Appendix D
Precision and Accuracy Data

Precision - precision will be expressed in terms of RPD of the duplicate results from the original results. The equation for expressing precision is:

RPD	=	$(D_1 - D_2)/[(D_1 + D_2)/2] \times 100$
where RPD	=	Relative Percent Difference
D_1	=	First Sample Value
D_2	=	Second Sample Value (duplicate)

Accuracy - accuracy will be expressed in terms of spiked samples. Recovery of the spike will be used to assess the data accuracy. Recovery is calculated as follows:

Rec	=	$[(D_s - D)/s] \times 100$
where Rec	=	Relative Percent Recovery
D_s	=	Value of sample with spike
D	=	Value of sample without spike
S	=	Amount of spike added

Appendix E
Acceptable Quality Control Limits at Stated Level
Sample Matrix Spike

Determination	%REC (Amount)	%RPD (ave Range)
MINERAL		
Alkalinity as $CaCo_3$ (titration)	88-111 (2.5 mg/L)	6.4 (390 mg/L)
pH 2.7 (7.0 units)		-
Specific Conductance (EC)	-	2.0 (718 units)
Dissolved Solids (TDS) @ 180°C	-	12 (30 mg/L)
Turbidity	-	5.0 (10 NTU)
Silica as SiO_2 (colorimetric)	83-113 (5.0 mg/L)	5.2 (25 mg/L)
Nitrate (automated, colorimetric)	78-118 (0.2 mg/L)*	4.3 (1.0 mg/L)*
Boron (automated, colorimetric)	92-111 (0.2 mg/L)	5.0 (1.0 mg/L)
Fluoride (electrode)	85-117 (0.5 mg/L)	5.0 (2.5 mg/L)
Chloride (automated, colorimetric)	89-114 (7.5 mg/L)	2.6 (37.5 mg/L)
Sulfate (automated, colorimetric)	82-120 (7.5 mg/L)	3.5 (37.5 mg/L)
Calcium (flame, AA)	84-117 (7.5 mg/L)	5.6 (37.5 mg/L)
Magnesium (flame, AA)	86-113 (7.5 mg/L)	3.0 (37.5 mg/L)
Potassium (flame, AA)	80-120 (1.5 mg/L)	2.5 (7.5 mg/L)
Sodium (flame, AA)	82-116 (10 mg/L)	2.3 (50 mg/L)
Total Suspended Solids	-	10 (12.5 mg/L)
Volatile Suspended Solids	-	13 (4.0 mg/L)
Bromide (IC)	82-118 (0.1 mg/L)	8.2 (0.5 mg/L)
UVA (254nm UV abs.)	-	5.1 (0.63 abs)
NUTRIENTS		
Total Kjedahl Nitrogen (automated,colorimetric)	74-127 (0.2 mg/L)	10.6 (1.0 mg/L)
Ammonia (automated, colorimetric)	86-118 (0.05 mg/L)	5.6 (0.25 mg/L)
Nitrite+Nitrate (automated, colorimetric)	79-119 (0.05 mg/L)	3.7 (0.25 mg/L)
ortho-phosphate as P (automated, colorimetric)	83-112 (0.05 mg/L)	4.0 (0.25 mg/L)

* as N

Determination	%REC (Amount)	%RPD (ave Range)
Total-phosphorus (automated, colorimetric)	81-118 (0.05 mg/L)	8.6 (0.25 mg/L)
METALS-FLAME AA		
Aluminum	81-117 (5.0 mg/L)	8.9 (10.0 mg/L)
Barium	82-118 (1.0 mg/L)	5.0 (2.5 mg/L)
Strontium	85-114 (1.0 mg/L)	3.6 (2.5 mg/L)
Iron	82-119 (1.0 mg/L)	8.2 (2.5 mg/L)
Lithium	85-115 (0.10 mg/L)	5.0 (1.0 mg/L)
Manganese	86-112 (1.0 mg/L)	5.1 (2.5 mg/L)
Nickel	85-115 (1.0 mg/L)	10.0 (2.5 mg/L)
METALS-HYDRIDE AND COLD VAPOR AA		
Arsenic (Hydride)	77-121 (5.0 µg/L)	12.0 (10 µg/L)
Selenium(Hydride)	74-121 (5.0 µg/L)	8.0 (10 µg/L)
Mercury (Cold Vapor)	80-120 (1.0 µg/L)	3.7 (1.0 µg/L)
METALS (DISSOLVED)		
Aluminum	83-120 (15 µg/L)	12.7 (37.5 µg/L)
Cadmium	87-119 (5 µg/L)	4.8 (12.5 µg/L)
Chromium	86-122 (5 µg/L)	6.6 (12.5 µg/L)
Copper	80-116 (5 ug/L)	6.6 (12.5 ug/L)
Iron	81-115 (5 µg/L)	8.0 (12.5 ug/L)
Lead	79-121 (5 µg/L)	5.0 (12.5 µg/L)
Manganese	85-115 (5 µg/L)	6.6 (12.5 µg/L)
Molybdenum	79-120 (5 µg/L)	5.6 (12.5 µg/L)
Nickel	83-120 (5 µg/L)	7.8 (12.5 ug/L)
Zinc	84-123 (5 µg/L)	8.0 (12.5 ug/L)
Cobalt	80-120 (5 µg/L)	7.0 (12.5 µg/L)
Silver	85-115 (5ug/L)	5.0 (5.0 ug/L)

Determination	%REC (Amount)	%RPD (ave Range)
METALS		
(TOTALS)		
Cadmium	76-120 (5.0 µg/L)	6.0 (12.5 µg/L)
Chromium	72-125 (5.0 µg/L)	12.0 (12.5 µg/L)
Copper	69-120 (5.0 µg/L)	12.0 (12.5 µg/L)
Lead	65-121 (5.0 µg/L)	12.0 (12.5 µg/L)
Manganese	71-120 (5.0 µg/L)	15.0 (12.5 µg/L)
Molybdenum	64-130 (5.0 µg/L)	17.0 (12.5 µg/L)
Silver	75-116 (5.0 µg/L)	5.0 (12.5 µg/L)
Zinc	68-128 (5.0 µg/L)	20.0 (12.5 µg/L)

Notes:

1. List is not complete; as data become available, results will be entered.
2. Organic data are being compiled at this time; currently using EPA QC limits.
3. Values listed are subject to change.
4. Limits were derived from surface, ground, and saline waters, and from agricultural wastewater.

Appendix F

Acceptable Quality Control Limits at Stated Level
Laboratory Control Sample

Determination	Warning Limit %	Control Limit %
MINERALS		
Calcium	90-110	85-125
Magnesium	90-110	85-125
Sodium	90-110	85-125
Potassium	90-110	85-125
Alkalinity	90-110	85-125
Sulfate	90-110	85-125
Chloride	90-110	85-125
Nitrate	90-110	85-125
Fluoride	90-110	85-125
Boron	90-110	85-125
Turbidity	90-110	85-125
Total Dissolved Solids	90-110	85-125
Specific Conductance	-	-
Silica	90-110	85-125
pH		90-110
85-125		
Bromide	90-110	85-125
Suspended Solids	-	-
Volatile Suspended Solids	-	-
TOC	90-110	85-125
NUTRIENTS		
Total Phosphorous	80-120	70-130
Total Kjeldahl Nitrogen	80-120	70-130
Dissolved ortho-phosphate	85-115	80-120
Dissolved Nitrate + Nitrite	85-115	80-120
DISSOLVED METALS		
Arsenic	85-115	80-120
Selenium	85-115	80-120
Mercury	85-115	80-120
Silver	90-110	85-115
Aluminum	90-110	85-115
Barium	90-110	85-115
Cadmium	90-110	85-115
Copper	90-110	85-115
Chromium	90-110	85-115
Iron	90-110	85-115
Manganese	90-110	85-115
Molybdenum	90-110	85-115
Lead	90-110	85-115
Nickel	90-110	85-115

Determination	Warning Limit %	Control Limit %
Vanadium	90-110	85-115
Zinc	90-110	85-115
TOTAL METALS		
All the above	85-115	80-120
Oil and Grease	75-125	70-130

Appendix G
Analytical Methods and Reporting Limits

Constituent		Method	Reporting Limit (mg/L)
MINERAL			
Calcium	EPA	215.1 AA Flame	1
		200.7 ICP	1
Magnesium		242.1 AA Flame	1
		200.7 ICP	1
Sodium		273.1 AA Flame	1
		200.7 ICP	1
Potassium		258.1 AA Flame	0.1
		200.7 ICP	0.5
Sulfate		375.2 Colorimetric, Methythymol Blue	1
		300.0 Ion Chromatography	1
Chloride	Std Methods	4500-Cl-E Colorimetric, Ferricyanide	1
Nitrate	EPA	300.0 Ion Chromatography	1
	EPA	353.2 Colorimetric, CD-Reduction	0.1
Fluoride	EPA	300.0 Ion Chromatography	0.01
Boron	EPA	200.7 ICP	0.1
Silica	EPA	200.7 ICP	0.5
Total Dissolved Solids	Std Methods	2540-C Gravimetric, Dried at 1800 C	1
	EPA	160.1 Gravimetric, Dried at 1800 C	1
Alkalinity	Std Methods	2320-B Titrimetric	1
	EPA	310.1 Titrimetric	1
pH	Std Methods	4500-H+ Electrometric	0.1 pH Unit
	EPA	150.1 Electrometric	0.1 pH Unit
Specific	Std Methods	2310-B Wheatstone Bridge	1 umhos/cm
Conductance	EPA	120.1 Wheatstone Bridge	1 umhos/cm
Turbidity	Std Methods	2130-B Nephelometric	1 NTU
	EPA	180.1 Nephelometric	1 NTU
UV Absorbance	Std Methods	5910-B UV-Absorbing Organics	0.001 abs/cm at 254nm

Constituent		Method	Reporting Limit (mg/L)
NUTRIENTS			
Ammonia	Std Methods	4500-NH_3 B,H Automated Phenate	0.01
	EPA	350.1 Automated Phenate	0.01
Total Kjedahl Nitrogen	EPA	351.2 Colorimetric, Semi-Automated	0.10
Nitrate	Std Methods	4500-NO_3-F Cd-Reduction	0.01
	EPA	353.2 Cd-Reduction, Automated	0.01
Nitrite	Std Methods	4500-NO_3-F Cd-Reduction	0.01
	EPA	353.2 Cd-Reduction, Automated	0.01
Nitrite + Nitrate	EPA	353.2, Cd-Reduction, Automated	0.01
o-Phosphate	Std Methods	4500-P-E Colorimetric, Ascorbic Acid	0.01
	EPA	365.1 Colorimetric, Ascorbic Acid	0.01
Phosphorus, Total	EPA	365.4 Colorimetric, Semi-Automated	0.01
METALS			
Aluminum	EPA	200.7 ICP	0.050
		200.8 ICP/MS	0.010
		200.9 GFAA	0.010
Antimony	EPA	200.7 ICP	0.025
		200.8 ICP/MS	0.001
Arsenic	Std Methods	3114 (4d), AA gaseous hybride	0.001
	EPA	200.7 ICP	0.050
		200.8 ICP/MS	0.001
Barium	EPA	200.7 ICP	0.010
		200.8 ICP/MS	0.050
		200.9 GFAA	0.050
		208.2 GFAA	0.050
Beryllium	EPA	200.7 ICP	0.010
		200.8 ICP/MS	0.001
		200.9 GFAA	0.005
		210.2 GFAA	0.005
Cadmium	EPA	200.7 ICP	0.010
		200.8 ICP/MS	0.001
		200.9 GFAA	0.005
		213.2 GFAA	0.005
Chromium (VI)	EPA	218.6 Ion Chromatography	0.005

Constituent		Method	Reporting Limit (mg/L)
Chromium (All valencies)	EPA	200.7 ICP	0.020
		200.8 ICP/MS	0.005
		200.9 GFAA	0.005
		218.2 GFAA	0.005
Cobalt	EPA	200.7 ICP	0.020
		200.8 ICP/MS	0.005
		200.9 GFAA	0.005
		219.2 GFAA	0.005
Copper	EPA	200.7 ICP	0.020
		200.8 ICP/MS	0.001
		200.9 GFAA	0.005
		220.1 AA Flame	0.10
		220.2 GFAA	0.005
Iron	EPA	200.7 ICP	0.025
		200.8 ICP/MS	0.005
		200.9 GFAA	0.005
		236.1 AA Flame	0.10
		236.2 GFAA	0.005
Lead	EPA	200.7 ICP	0.050
		200.8 ICP/MS	0.001
		200.9 GFAA	0.005
		239.2 GFAA	0.005
Lithium	USGS	I-1425-85 AA Flame, Direct	0.10
	EPA	200.8 ICP/MS	0.005
Manganese	EPA	200.7 ICP	0.010
		200.9 GFAA	0.005
		243.1 AA Flame	0.10
		243.2 GFAA	0.005
Mercury	EPA	245.1 AA, Flameless, Cold Vapor	0.001
Molybdenum	EPA	200.7 ICP	0.020
		200.8 ICP/MS	0.005
		200.9 GFAA	0.005
		246.2 GFAA	0.005
Nickel	EPA	200.7 ICP	0.025
		200.8 ICP/MS	0.001
		200.9 GFAA	0.005
		249.1 AA Flame	0.10
		249.2 GFAA	0.005

Constituent		Method	Reporting Limit (mg/L)
Selenium	Std Methods	3114B AA gaseous hydride	0.001
	EPA	200.8 ICP/MS	0.001
Silver	EPA	200.7 ICP	0.025
		200.8 ICP/MS	0.001
		200.9 GFAA	0.005
		272.2 GFAA	0.005
Thallium	EPA	200.7 ICP	0.10
		200.8 ICP/MS	0.001
		200.9 GFAA	0.002
		279.2 GFAA	0.002
Vanadium	EPA	200.7 ICP	0.020
		200.8 ICP/MS	0.005
		200.9 GFAA	0.010
		286.2 GFAA	0.010
Zinc	EPA	200.7 ICP	0.020
		200.8 ICP/MS	0.005
		200.9 GFAA	0.005
		289.1 AA Flame, Direct	0.10
		289.2 GFAA	0.005
Strontium	EPA	200.8 ICP/MS	0.005
MISCELLANEOUS			
Settleable Solids	Std Methods	2540-F, Volumetric, Imhoff	0.10
	EPA	160.5 Volumetric, Imhoff	0.10
Suspended Solids	Std Methods	2540-D, Gravimetric, 105° C	0.10
	EPA	160.2 Gravimetric, 105°C	0.10
Color	Std Methods	2120-B, Visual Comparison, Pt-Co	5 Color Units
	EPA	110.2 Colorimetric, Pt-Co	5 Color Units
Surfacants, MBAS	Std Methods	5540-C, Colorimetric	0.10
	EPA	425.1 Colorimetric	0.10
COD Chemical Oxygen Demand	EPA	410.2 Titrimetric, low-level	1.0
Oil and Grease	Std methods	5520-B, Gravimetric	5.0
	EPA	1664 Gravimetric	5.0
BOD Biological Oxygen Demand	EPA	405.1 Incubation, 20°C	0.10

Constituent		Method	Reporting Limit (mg/L)
Organic Carbon (TOC)	Std Methods	5310-D, Wet Oxidation, IR, Automated	0.10
	EPA	415.1 Wet Oxidation, IR, Automated	0.10
	EPA	415.1 Combustion, IR, Automated	0.10
Tannin & Lignin	Std Methods	5550-B, Colorimetric	0.10
Volatile	Std Methods	2540-E, Gravimetric, 500^{o} C	0.10
Suspended Solids			
	EPA	160.4 Gravimetric, 500^{o}C	0.10
ORGANICS			
Trihalomethane Potentials (THMFP)	EPA	510.1 (Modified) GC, Purge and Trap	1.0
1,2-Dibromoethane (EDB)		504 Gas Chromatography (GC)	0.02
1,2-Dibromo-3-Chloropropane (DBCP)		504 Gas Chromatography (GC)	0.01
Volatile Organics		502.2 Purge and Trap	0.5
Carbamates		531.1 High Pressure Liquid Chromatography (HPLC)	2.0-4.0
Glyphosate		547 HPLC	100.0
Haloacetic Acids		552.2 Gas Chromatography (GC)	1.0
Chlorinated Pesticides		608 Gas Chromatography (GC)	0.01-1.0
Nitrogen/Phosphorus Pesticides		614 Gas Chromatography (GC)	0.01-5.0
Chlorinated Phenoxy Acids (Herbicides)		615 Gas Chromatography (GC)	0.1-1.0

Appendix H
Laboratory Equipment

Organic Section	Quantity
Hewlett Packard Model 5973 GCMS with purge and trap and large volume injection capability	1
Finnigan INCOS 50 GCMS with purge and trap and split/splitless capability	1
Hewlett-Packard model 5890II GC with megabore capillary column, OI 4420 electrical conductivity detector and a photoionization detector	1
Hewlett-Packard model 5890II GC with capillary column, an OI 4420 electrical conductivity detector and photoionization detector	1
Hewlett-Packard model 5890II GC with dual capillary columns and electron capture detectors	1
Hewlett-Packard model 5890II GC with dual megabore capillary columns, flame photometric detector, nitrogen-phosphorus detector and Hewlett-Packard auto-sampler	1
Hewlett-Packard model 5890II GC with dual capillary columns, two OI 4420 electrical conductivity detectors, and Hewlett-Packard auto-sampler	1
Tekmar LSC 2000 purge and trap concentrator with a Tekmar ALS2016 automatic laboratory sampler 16 position liquid sparge unit	1
Tekmar LSC 2 purge and trap concentrator with a Tekmar ALS automatic laboratory sampler 16 position sparge unit	2
Tekmar LSC2 purge and trap concentrator with a single sparge unit	1
Kratos HPLC system with three Spectroflow 400 pumps capable of gradient programming, Spectroflow 980 Fluorescence detector, BIO-RAD autosampler and a Kratos 520 post column heater	1
Spectro-physics model SP4290, HPLC data operating system	1
OIC model 700 TOC analyzer with model SHLR autosampler and Microline 182 printer	1
OIC model 1010 persulfate wet oxidation total organic carbon analyzer with an OIC 1051 vial multisampler	1
OIC model 1020A combustion total organic carbon analyzer with an OIC 1051 vial autosampler	1
OIC ampule TOC purge and sealing unit	1
Agilent model 1100 HPLC with diode array and fluorescence detectors, in-line degasser and autosampler	1
Pickering Laboratories model PCX 5200 post column derivatizer	1
Horizon model 4900 automated liquid solid phase extractor	1

Inorganic Section	Quantity
Perkin-Elmer Elan 6000 ICP/MS with a PE AS-91 autosampler	1
Perkin-Elmer 5000 atomic absorption spectrophotometer with a PE AS-50 autosampler and PE printer	1
Varian Spectra 55 AA with a SPS-5 sample preparation system	1
Perkin-Elmer model 50A cold vapor mercury analyzer and chart recorder	1
Perkin-Elmer model Optima 4300 DV ICP with a PE S-90 autosampler	1
Technicon Auto Analyzer II system consisting of an autosampler, pump, manifold, colorimeter and chart recorder	6
Lachat model 8000 flow injection analyzer (FIA) with a XYZ autosampler	1
Alpkem RFAC Auto Analyzer Data System consisting of dual disc drive multi-tasking control and data processing system with Okidata Microline 83A printer/plotter	1
Bran+Luebbe Traccs 800 continuous-flow analytical system consisting of random access sampler, analytical console, IBM computer and printer/plotter	1
Fisher computer aided titrimeter consisting of the model 450 titration controller, model 455 titration burette, model 460 stirrer, model 489 rotary multisampler and printer	1
Bausch and Lomb Spectronic 88 UV-Vis Spectrophotometer	1
Dionex ion chromatograph (IC) system with gradient pump, variable wavelength detector, conductivity detector Bio-Rad AS60 auto sampler and spectra physics SP 4270 integrator	1
Perkin-Elmer Lambda 11 UV/VIS Spectrometer with autosampler	1
Metrohm autotitrator with a 712 conductometer, 719 titrator and a 745 autosampler	1
Dionex ion chromatograph (IC) with gradient pump, electrochemical conductivity detectors and an A540 sampler	2

Biological Section	Quantity
Perkin-Elmer model Lambda 40 UV-Vis Scanning Spectrophotometer	1
Colilert fecal coliform testing equipment consisting of a quanti-tray sealer, thermolyne incubator and a long wavelength lamp	1
Wild Heerbrugg inverted microscope with a Nikon camera attachment	1

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